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THE CHEMICAL EFFECT OF GYPSUM, SULFUR, IRON SULFATE, AND ALUM ON ALKALI SOIL¹

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INTRODUCTION

Until recently the toxicity of alkali soils was attributed almost exclusively to the presence of an excess of one or more of the soluble salts, and the general opinion has been that the toxic conditions will be removed by leaching out the soluble salts. Where sodium carbonate occurs Hilgard pointed out that it may be necessary to apply some substance, such as gypsum, which will convert the carbonate into a neutral salt; otherwise it may be difficult or even impossible to leach out the soluble salts, owing to the deflocculated condition of the soil that is produced by alkali carbonates. In any case the prevailing opinion has been that the removal of the soluble salts will overcome the toxic conditions. Numerous attempts have been made to reclaim alkali soils by applying this idea. In some instances good success has been obtained; in others the results have been disappointing.

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³ Chemical Engineer of the Royal Hungarian Agrochemical Experiment Station, Debrecen, Hungary. The chemical studies reported in this paper were carried out by the junior author while working in the Citrus Experiment Station under a Fellowship granted by the International Education Board. These data were first discussed in a manuscript which the junior author prepared for publication in Hungary. Since the form and method of treatment employed therein seemed to be not well suited for publication in California, it was decided to write an entirely new manuscript. The interpretation of the data and general conclusions that are drawn are similar in these two papers.

Investigations on the base-exchange phenomenon during the past fifteen years have thrown important light on this question. Whereas the older idea presupposed that the soluble salts are commingled with and form a mere mechanical mixture with the insoluble constituents of the soil, these base-exchange investigations have shown that under certain conditions the soluble salts produce substantial chemical changes in certain components of the clay constituents of the soil, and that these changes are as important as and even more difficult to overcome than the soluble salts. Ordinary leaching may remove the latter, but the leaching process will not bring about the needed chemical change in the former.

The inorganic base-exchange constituents of non-alkali soils, sometimes referred to as zeolites, are chiefly calcium and magnesium compounds, with the former usually present in much the greater amount. On the other hand, sodium compounds predominate among the soluble salts of alkali soils; not infrequently the soluble salts are composed almost entirely of sodium compounds. As the sodium salts accumulate during the course of alkali-soil formation, the sodium reacts with the base-exchange constituents of the soil, replacing more or less calcium and magnesium and forming simple salts of these bases and sodium-exchange compounds. We now know that alkali soil which contains an excess of replaceable sodium is likely to be more or less toxic to plants even after the excess of soluble salts has been leached out.

It follows, therefore, that in addition to the removal of the excess of soluble salts, the successful reclamation of an alkali soil may necessitate the displacement of a part, at least, of the replaceable sodium. In fact the reclamation will probably not be truly complete until practically all of the exchangeable sodium has been replaced, although, as will be shown later, satisfactory crops may be grown when sodium does not comprise too high a percentage of the total replaceable bases.

Where neutral sodium salts accumulate, the exchange of bases rarely, if ever, goes to completion, owing to the nature of the equilibrium. On the other hand, if carbonate is a constituent of the soluble salts, as is often the case in black-alkali soils, the replaced calcium will be precipitated as the carbonate, and the magnesium probably as the basic carbonate, which precipitation will materially affect the equilibrium. In this case, especially if the total concentration of sodium salts is high, a large percentage of the base-exchange constituents will be converted into sodium compounds and the replaced

calcium and magnesium will be precipitated in the soil as carbonates. If potassium is a constituent of the accumulated soluble salts, this element will also participate in the base-exchange reactions with the formation of more or less of potassium-exchange compounds. The presence of soluble calcium, on the other hand, materially affects the replacement of soil bases by sodium salts, and if present in sufficient concentration, soluble calcium may prevent the replacement of calcium from the exchange complex even though the total concentration of sodium salts is high.⁴

On the basis of the results of studies on the general principles of base exchange,^(6, 8, 16) and of the study of several types of alkali soils, Kelley and Brown⁽¹³⁾ pointed out that a determination of (a) the water-soluble cations, especially calcium and sodium, (b) the replaceable bases, (c) the OH-ion concentration of the soil and (d) the composition of the irrigation water together make it possible to predict whether leaching alone will bring about successful reclamation.

Whether the exchange complex has been only partially or wholly converted into sodium compounds through the exchange of bases, this complex is not removed from the soil by ordinary leaching with water; neither will moderate leaching convert these sodium compounds into calcium compounds except under special conditions and then the conversion will usually be only partial. It follows, therefore, that the mere leaching and drainage of an alkali soil may not produce satisfactory reclamation.

In connection with field experiments, which the University of California has been conducting for several years on alkali soil near Fresno, California, different materials have been applied. Some of these materials have produced marked improvement in the growth and yield of crops, whereas leaching with water without other treatment has not produced satisfactory results. Since previous investigations^(12, 13) have shown that sodium comprises a relatively high percentage of the total replaceable bases of this soil and that there is an excess of soluble sodium salts present, including sodium carbonate, it is a matter of special interest to study the chemical changes that

⁴In this paper it is assumed that, apart from the soluble salts, an alkali soil represents materials which once were similar to those of a non-alkali soil of the same type, but which have since been acted on by soluble salts. Whether the soluble salts acted on the soil materials before or after the latter were laid down in their present location is perhaps inconsequential, in so far as this discussion is concerned. As a matter of fact the sodium salts, including the carbonate, accumulated in the area under consideration some time later than 1890 in consequence of seepage and poor drainage. Before that time this soil was free from an excess of salts and produced successful crops of various kinds.

have been brought about in the soil both as regards the replaceable bases and the soluble salts, and to attempt to correlate these changes with the crop responses. A description of the field experiments, including a record of the treatments and the crop yields, is given in a separate paper.⁽¹⁸⁾ The present paper will be devoted to a consideration of the chemical changes that have been produced in the soil.

The following plots have been investigated: Plot 4, treated in 1920 with 9 tons per acre of gypsum and again in 1921 with 6 tons per acre of gypsum; plot 10, treated in 1921 with 3600 pounds per acre of finely ground elemental sulfur; plot 11, treated in 1921 with 10 tons per acre of gypsum; plot 17, treated in 1922 with 9 tons per acre of ferrous sulfate; plot 18, treated in 1923 with 10 tons per acre of potassium alum; plot 19, treated in 1922 with 20 tons per acre of stable manure and in 1925 with 1000 pounds per acre of elemental sulfur, and plot 45, treated in 1925 with 5 tons per acre of ferrous sulfate.

Each of these plots was sampled before the materials were applied and again after the lapse of two or more years. The samples (14 or more) were taken at intervals of ten feet across the greatest diameter of each plot. In the interval between the sampling dates the plots were heavily flooded at certain times in order to leach out the soluble salts and to assist in making the treatments effective. All of the plots have been irrigated freely whenever any crop was being grown. These samples have been analyzed individually for soluble salts and the results are being reported elsewhere.⁽¹⁸⁾ Recently a series of composite samples were prepared by mixing, for each such sample, equal quantities of the individual samples that were drawn from a given plot, and these composites were used in the present study.

It should be pointed out in this connection that when the plot experiments were first begun the content of soluble salts was by no means the maximum concentration that this soil had previously contained. The quarter section (160 acres), of which these experimental plots comprise only a part, was flooded and kept covered with water for a period of two or more months in the summer of 1914 and again in 1915,⁽²¹⁾ in what has proved to be an unsuccessful attempt to reclaim the land by flooding and drainage. Although the total concentration of soluble salts in the various parts of this area before it was flooded is not known definitely, it is certain that very much of the salts was then leached out. When the plot experiments were begun the soil was extremely toxic to plants, previous plantings of barley and alfalfa having failed to germinate over a large part of the experimental area.

The soil is a fine sandy loam the upper horizon of which contains a small but variable amount of calcium carbonate. The texture is practically uniform down to a depth of two or more feet, where a compacted layer resembling hardpan is found. This layer, the thickness of which ranges from two to six or more inches, contains considerable insoluble carbonate (chiefly calcium carbonate). This layer is hard and difficult to penetrate when dry, but water readily passes through it, and when it is wet the soil auger cuts through without difficulty. Beneath this calcareous layer many similar layers, separated from each other by soil and clay materials, occur down to a depth of fifty or more feet. In certain places the uppermost calcareous layer occurs at a depth of about two feet, while a few inches away it may be three or four feet below the surface. Because of this fact the two sets of soil samples from certain of the experimental plots, especially those representing the third and fourth feet in depth, were found to vary considerably in their content of insoluble carbonate.

The methods used in this study were those which have been elaborated and employed in the laboratory of the Citrus Experiment Station for several years. The samples were analyzed for water-soluble constituents, total carbonate, replaceable bases and hydrogen-ion concentration. The soluble constituents were determined by shaking 200 grams of soil with 1000 cc. of distilled water for one hour, filtering and analyzing the filtrate. Total carbonate was determined gravimetrically by boiling 10 grams of soil with dilute sulfuric acid and absorbing the CO_2 in potash bulbs. The replaceable bases were determined by a modification of the ammonium chlorid method, which is discussed in another paper,⁽¹⁵⁾ and the pH values were determined on a suspension of the soil by means of the hydrogen electrode.

EFFECT ON THE SOLUBLE SALTS

In agreement with the results of previous studies on this area⁽¹¹⁾, the analyses presented in tables 1-7 show that the initial distribution of water-soluble salts was variable in these plots. This is especially true as regards the normal carbonate, the concentration of which was originally the highest in the surface soil of each plot. With plots 4, 10 and 11 considerable soluble carbonate was found down to a depth of four feet, while below the depth of two feet plots 18 and 45 contained much less soluble carbonate and the same was true of the fourth foot of plots 17 and 19. It was only in the case of the third and fourth feet of plot 18 that the original samples contained any appreciable amount of soluble calcium and magnesium.

The data show that the content of water-soluble salts in the upper horizon of each plot has been materially reduced by each of the treatments. However, certain soluble constituents, notably sodium, sulfate and carbonate, have been increased in the third and fourth feet of certain plots. This is due chiefly to the leaching down of soluble substances from the upper layers. Those plots which were most thoroughly leached (plots 4, 10 and 11) have been almost completely freed from chlorid down to the depth of at least four feet, whereas considerable chlorid still remains in the deeper layers of the other plots. For example, in the case of plots 19 and 45, which have been leached only moderately, chlorid has markedly accumulated in the fourth foot. In the case of the first foot of plots 4, 10 and 11, the treatments have produced notable increases in the content of soluble calcium and magnesium.

TABLE 1

PLOT 4, TREATED WITH 15 TONS GYPSUM PER ACRE;
WATER-SOLUBLE CONSTITUENTS
(Milliequivalents per 100 grams.)

	0-12 inches		12-24 inches		24-36 inches		36-48 inches	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
CO ₂	1.04	tr	0.71	0.35	0.66	0.36	0.56	0.43
HCO ₃	1.11	0.38	1.04	0.61	0.79	0.56	0.71	0.62
Cl.....	0.14	0.06	0.31	0	0.33	0	0.27	0
SO ₄	0.73	0.39	0.55	0.24	0.32	0.25	0.25	0.25
Ca.....	tr	0.47	tr	tr	tr	tr	tr	tr
Mg.....	tr	0.25	tr	tr	tr	tr	tr	tr
K.....	0	0	0	0	0	0	0	0
Na.....	3.01	0.12	2.61	1.19	2.10	1.18	1.77	1.29

The chlorid determinations, when considered in connection with the amount of water that has been applied, show that it is possible to remove the soluble neutral salts from this soil by leaching. It is even possible, as shown by special leaching experiments, to remove practically all of the soluble carbonate. On the other hand, moderate leaching may actually increase the amount of soluble carbonate. This, as was shown by Gedroiz⁽⁷⁾ and others⁽¹³⁾ is due chiefly to the fact that, upon lowering the concentration of soluble sodium, calcium carbonate reacts with the sodium-exchange complex, forming calcium-exchange complex and sodium carbonate. This reaction is promoted

by carbon dioxid because of its influence on the OH-ion concentration and its solvent power for calcium carbonate. If an abundance of carbon dioxid is present, the soluble end-product of this reaction will be bicarbonate rather than the normal carbonate. This effect of calcium carbonate and carbon dioxid is a very important one and should be utilized to the fullest extent possible in the reclamation of black-alkali soil. This question will be discussed at greater length in a separate paper that will be devoted to a consideration of the effects of leaching as such.

TABLE 2
PLOT 10, TREATED WITH 3600 POUNDS SULFUR PER ACRE;
WATER-SOLUBLE CONSTITUENTS
(Milliequivalents per 100 grams.)

	0-12 inches		12-24 inches		24-36 inches		36-48 inches	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
CO ₂	1.14	0.00	0.54	0.00	0.66	0.60	0.34	0.93
HCO ₃	1.60	0.75	1.04	0.75	1.23	1.03	1.00	1.14
Cl.....	1.53	0.00	1.20	0.00	0.68	tr	0.53	0.23
SO ₄	0.99	0.44	0.53	0.45	0.15	0.64	0.08	0.62
Ca.....	tr	0.46	tr	tr	0	0	0	0
Mg.....	tr	0.35	tr	tr	0	0	0	0
K.....	0.02	0.00	0	0	0	0	0	0
Na.....	5.24	0.38	3.30	1.19	2.72	2.26	1.94	2.91

TABLE 3
PLOT 11, TREATED WITH 10 TONS GYPSUM PER ACRE;
WATER-SOLUBLE CONSTITUENTS
(Milliequivalents per 100 grams.)

	0-12 inches		12-24 inches		24-36 inches		36-48 inches	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
CO ₂	1.19	tr	0.89	0.69	0.71	1.34	0.40	1.27
HCO ₃	1.23	0.62	0.97	0.98	1.01	1.03	0.78	1.09
Cl.....	1.33	0.15	1.08	0	0.78	0	0.59	0.20
SO ₄	0.20	0.43	0.21	0.29	0.18	0.24	0.15	0.26
Ca.....	tr	0.19	tr	tr	tr	tr	tr	tr
Mg.....	tr	0.22	tr	tr	tr	tr	tr	tr
K.....	0.05	0	0	0	0	0	0	0
Na.....	3.90	0.86	3.14	1.97	2.67	2.61	1.92	2.81

It will be noted that in the case of plot 10, which was treated in 1921 with 3600 pounds of sulfur per acre, there has been a complete removal of soluble carbonate to a depth of two feet. On the other hand, plot 19, which was treated in 1922 with 20 tons per acre of manure and in 1925 with only 1000 pounds per acre of sulfur, has not been so completely freed from soluble carbonate. Each of these treatments has caused a slight increase in the soluble carbonate in the deeper subsoil. This, as suggested above, was probably due chiefly to the leaching down of carbonates from the upper layers. It is especially interesting to see that no appreciable increase in soluble carbonate has taken place in the subsoil of the plot that was treated with a large amount of a substance, which converts soluble carbonate into insoluble calcium carbonate (gypsum, plot 4), or which decomposes carbonate (iron sulfate, plot 17, and alum, plot 18). On the other hand, the subsoil of those plots which were treated with a smaller amount of these materials (plot 11, treated with 10 tons per acre of gypsum, and plot 45, treated with 5 tons per acre of iron sulfate) has sustained an increase in soluble carbonate. It seems that these last named amounts of gypsum and iron sulfate were insufficient to precipitate or decompose all of the soluble carbonate in the upper layers of this soil. As was shown previously,^(17, 20) gypsum and iron sulfate react on the soluble carbonate and the sodium-exchange compounds simultaneously. The consequence is that the amount of these materials that must be applied is not determined solely and in some cases not even chiefly by the content of soluble carbonate.⁵

The data strongly suggest that where sulfur is applied to an alkali soil in which the soluble carbonate is largely concentrated near the surface, excessive leaching should be delayed until active oxidation has taken place. In this event the oxidation products will decompose the soluble carbonate, whereas heavy leaching during the earlier stages of the oxidation will tend to wash more or less of the soluble carbonate into the subsoil, just as has been the case in certain of these plots.

⁵ In this connection it is of interest to note that Burgess⁽⁴⁾ and his colleagues^(2, 3) have concluded from their studies on Arizona alkali soils that sodium carbonate is non-existent in black alkali soils in general. They attribute the alkalinity of this type of soil to hydrolysis of the sodium-exchange complex, rather than to sodium carbonate. Although the sodium complex does undergo more or less hydrolysis, as was discussed in detail several years ago by Gedroiz,⁽⁷⁾ Cummins and Kelley⁽⁶⁾ and others, there is abundant evidence that sodium carbonate actually occurs in certain black-alkali soils. For example, the displaced soil solution of a sample drawn from an unleached portion of the Fresno experimental area was found to contain 2250 p.p.m. CO_3 , and its pH was 9.11. It is evident that this soil must contain normal carbonate.

Soluble carbonate produces a condition in soils which is extremely toxic to plants and this substance should be completely removed from the soil if possible. If sodium carbonate is leached down into the subsoil, capillarity may cause it to rise toward the surface at some later time. Moreover, the accumulation of soluble carbonate in the subsoil tends to prevent the development of a deep root system by plants.

TABLE 4
PLOT 17, TREATED WITH 9 TONS FeSO_4 PER ACRE;
WATER-SOLUBLE CONSTITUENTS
(Milliequivalents per 100 grams.)

	0-12 inches		12-24 inches		24-36 inches		36-48 inches	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
CO_2	1.38	0.00	0.50	0.22	0.30	0.30	0.11	0.10
HCO_2	1.43	0.95	0.88	0.97	0.76	0.97	0.68	0.85
Cl.....	1.11	0.13	0.59	0.21	0.50	0.45	0.31	0.40
SO_4	0.57	0.39	0.33	0.32	0.25	0.60	0.18	0.68
Ca.....	tr	0	0	0	0	tr	0	0.18
Mg.....	tr	0	0	0	0	tr	0	0.34
K.....	0	0	0	0	0	0	0	0
Na.....	4.49	1.48	2.29	1.71	1.80	2.31	1.27	1.51

TABLE 5
PLOT 18, TREATED WITH 10 TONS ALUM PER ACRE;
WATER-SOLUBLE CONSTITUENTS
(Milliequivalents per 100 grams.)

	0-12 inches		12-24 inches		24-36 inches		36-48 inches	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
CO_2	1.30	0.00	0.40	0.05	0.32	0.08	0.21	0.00
HCO_2	1.34	0.88	0.98	0.85	0.96	0.86	0.93	0.77
Cl.....	0.83	0.15	0.51	0.24	0.51	0.48	0.47	0.34
SO_4	0.49	0.34	0.30	0.58	0.49	1.04	0.54	1.17
Ca.....	0	0	0	0	0.24	0.25	0.18	0.38
Mg.....	0	0	0	0	0.21	0.36	0.17	0.39
K.....	0	0	0	0	0	0	0	0
Na.....	3.96	1.36	2.18	1.70	1.89	1.84	1.85	1.51

TABLE 6

PLOT 19, TREATED WITH 20 TONS MANURE PER ACRE AND 1000 POUNDS SULFUR
PER ACRE; WATER-SOLUBLE CONSTITUENTS
(Milliequivalents per 100 grams.)

	0-12 inches		12-24 inches		24-36 inches		36-48 inches	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
CO ₂	1.15	0.33	0.50	0.72	0.23	0.36	0.03	0.13
HCO ₃	1.72	0.87	1.12	0.99	1.01	0.84	1.01	0.74
Cl.....	1.29	0.18	0.76	0.41	0.60	0.95	0.93	1.02
SO ₄	0.64	0.62	0.19	0.82	0.20	1.14	0.23	0.97
Ca.....	tr	0	tr	tr	tr	tr	tr	0.32
Mg.....	tr	0	tr	tr	tr	tr	tr	0.46
K.....	0.07	0	0.03	0	0	0	0	0
Na.....	4.73	2.00	2.53	2.92	2.04	3.29	2.19	2.08

TABLE 7

PLOT 45, TREATED WITH 5 TONS FeSO₄ PER ACRE;
WATER-SOLUBLE CONSTITUENTS
(Milliequivalents per 100 grams.)

	0-12 inches		12-24 inches		24-36 inches		36-48 inches	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
CO ₂	0.58	0.10	0.29	0.52	0.10	0.51	0.03	0.10
HCO ₃	1.32	0.80	1.01	0.95	0.79	0.95	0.80	0.63
Cl.....	1.46	0.15	0.60	0.20	0.48	0.38	0.43	0.90
SO ₄	0.38	0.18	0.13	0.17	0.06	0.75	0.10	0.79
Ca.....	tr	0	tr	0	tr	tr	tr	0.34
Mg.....	tr	0	tr	0	tr	tr	tr	0.50
K.....	0.03	0	0	0	0	0	0	0
Na.....	3.70	1.23	2.03	1.83	1.44	2.58	1.35	1.56

EFFECT ON THE INSOLUBLE CARBONATE

The data reported in table 8 show that the original carbonate content of plot 4 was approximately the same throughout the four feet in depth, whereas the third and fourth feet of the other plots contained much more carbonate than the first and second feet. It will be noted that the application of gypsum (plots 4 and 11) has produced an increase in the insoluble carbonate of the first foot, while the application of sulfur (plots 10 and 19), iron sulfate (plots 17 and 45) and alum (plot 18) has caused a decrease. In the case of plot 10, which was treated with a relatively large amount of sulfur, and of plot 18, treated with a heavy application of alum, the insoluble carbonate of the second foot has also sustained some loss. On the other hand, it is improbable that any of these treatments have materially affected the insoluble carbonate of the third and fourth feet. It is probable that the differences in the amount of insoluble carbonate found in the two sets of samples representing the third and fourth feet of a given plot were not produced by the treatments, but were due to the inherent variability of the subsoil. This variation seems to be closely related to the sporadic fluctuation in the thickness of and depth to the compacted calcareous layers previously mentioned.

TABLE 8
EFFECT ON THE CONTENT OF INSOLUBLE CO₂
(Milliequivalents per 100 grams.)

Depth in inches	Plot 4		Plot 10		Plot 11		Plot 17	
	Before treatment	After treatment with gypsum	Before treatment	After treatment with sulfur	Before treatment	After treatment with gypsum	Before treatment	After treatment with iron sulfate
0-12	5.49	6.33	4.09	1.22	8.20	8.82	4.68	3.18
12-24	4.01	4.11	2.97	2.25	6.81	6.91	3.72	3.67
24-36	5.19	4.19	21.29	21.47	25.46	18.22	33.01	38.10
36-48	3.40	3.06	32.34	33.43	35.56	35.33	46.70	33.65

Depth in inches	Plot 18		Plot 19		Plot 45	
	Before treatment	After treatment with alum	Before treatment	After treatment with sulfur	Before treatment	After treatment with iron sulfate
0-12	8.33	5.43	5.70	3.66	4.73	3.21
12-24	8.96	8.44	3.85	3.84	4.63	4.62
24-36	52.69	67.00	18.07	23.07	14.69	15.50
36-48	64.08	43.79	46.70	44.05	20.56	31.57

The effects of the several treatments on the insoluble carbonates are in close agreement with the theoretical probabilities that have been discussed in previous publications.^(13, 17, 20) For example, gypsum reacts with the soluble carbonate to form calcium carbonate, thus bringing about an increase in the content of insoluble carbonate. On the other hand, sulfur becomes oxidized to sulfuric acid, and both iron sulfate and alum are acidic compounds by virtue of their hydrolytic nature. The consequence is that the application of these materials brings about a conversion of both the soluble and insoluble carbonates into bicarbonate and sulfate, or else a decomposition of carbonates with the consequent evolution of carbon dioxide. When acidic types of material, such as sulfur, iron sulfate, etc., are applied, the resulting reactions bring more or less calcium carbonate into solution and therefore increase the content of soluble calcium. This is an extremely important step in the reclamation process, as has been pointed out in previous publications.^(13, 17) In fact the practical value of these materials rests in considerable part on their action upon calcium carbonate, as will be more fully discussed later.

EFFECT ON THE REPLACEABLE BASES

As is well known the solubility factor complicates the determination of the replaceable bases in any soil. If the total content of replaceable bases is low and if certain other types of calcium and magnesium compounds are present, the amount of calcium and magnesium that is dissolved by the salt solution used in the determination of the replaceable bases may exceed the total quantity of bases that is actually replaced by the base of the salt solution. This fact is especially important in the study of certain types of alkali soil. Calcium carbonate is a common constituent of black-alkali soils, and, under certain circumstances, normal magnesium carbonate may also be present. Moreover, as was pointed out previously,⁽¹³⁾ it is possible that the basic carbonate of magnesium may be formed as a result of base exchange, if soluble carbonate is present. As is well known these carbonates are distinctly soluble in ammonium chlorid, the salt that is commonly used in the determination of the replaceable bases. Gedroiz pointed out⁽⁹⁾ that the error in the determination of replaceable calcium caused by calcium carbonate can be calculated from the determination of the total carbonate before and after extracting the replaceable bases. Obviously it is permissible to introduce this correction only where calcium carbonate is the only carbonate present.

In addition to the various carbonates, previously published data⁽¹³⁾ strongly indicate that black-alkali soils may contain appreciable amounts of calcium or magnesium silicates which become soluble in the course of the determination of the replaceable bases. Where a mixture of these various carbonates and silicates occurs, we know of no method by which it is possible to make an accurate determination of the replaceable calcium or magnesium.

However, it is reasonably certain that the exchange of ions which takes place between a salt solution and the exchange complex of the soil is a stoichiometric process. For each ion that is replaced from the soil by a given treatment a chemical equivalent of some other ion must be absorbed by the soil. Therefore, the amount of base that a soil absorbs from the neutral salt solution that is used in the determination of the replaceable bases must be equivalent to the total quantity of ions that is replaced by the base of that salt. If the soil is neutral or alkaline, its exchangeable cations are confined chiefly to the replaceable bases. Hence, by thoroughly leaching the soil with a salt solution, whose base was not originally present in the soil and does not form insoluble compounds with the constituents of the soil other than the exchange components,⁶ and then by making a determination of the amount of this base that is absorbed, we have an indirect method for the determination of the total content (S) of replaceable bases. The quantity thus found, expressed as chemical equivalents, less the sum of the replaceable potassium and sodium, gives a measure of the replaceable divalent bases. Using this method of calculation Kelley and Brown⁽¹³⁾ concluded that certain black-alkali soils were saturated with monovalent base. Obviously this method does not enable us to say whether the replaceable divalent base is calcium or magnesium or both. We have used this method in the present study.

The procedure adopted in this study was as follows: After digesting 25 grams of soil over night at 70° C. with 250 cc. normal ammonium chlorid, the sample was thrown on a filter and leached to one liter with normal ammonium chlorid. The leachate was then analyzed for bases. The soil remaining on the filter was freed from ammonium chlorid by leaching with methyl alcohol as proposed by Kelley and Brown,⁽¹⁵⁾ ⁷ and then the absorbed NH_4 was determined by distillation in the presence of an alkali. The amount of absorbed NH_4 is assumed to be equivalent to the sum of all the bases that have been replaced. Leach-

⁶ It is doubtful whether the barium chlorid method as proposed by Burgess and Breazeale⁽⁵⁾ fulfills this requirement.

⁷ This method was discussed at the Meeting of the International Society of Soil Science held in Washington, D. C., June, 1927.

ing with methyl alcohol makes it possible to remove the occluded ammonium chlorid without danger of loss of the absorbed NH_4 through hydrolysis, and the coagulating effect of the alcohol prevents the leaching out of colloidal materials. When water is used to leach out the ammonium chlorid, more or less colloidal material may pass through the filter paper. With soils which contain considerable organic matter it may be necessary to make a correction in the NH_4 data by distilling the original soil, but this is not important with the Fresno soil.

TABLE 9
EFFECT OF GYPSUM ON THE REPLACEABLE BASES
(Milliequivalents per 100 grams.)

Plot 4										
Depth in inches	Before treatment					After treatment				
	K	Na	Ca+Mg	Total (S)	Na as per cent of total	K	Na	Ca+Mg	Total (S)	Na as per cent of total
0-12	0	3.70	1.10	4.80	75	0	1.78	3.17	4.95	36
12-24	0	3.42	1.52	4.94	69	0	2.00	2.95	4.95	40
24-36	0	2.39	2.53	4.92	49	0	2.57	2.32	4.89	53
36-48	0	2.01	3.22	5.23	38	0	3.13	2.28	5.41	58

Plot 11										
Depth in inches	Before treatment					After treatment				
	K	Na	Ca+Mg	Total (S)	Na as per cent of total	K	Na	Ca+Mg	Total (S)	Na as per cent of total
0-12	0.49	3.44	1.12	5.05	68	0.11	1.97	2.92	5.00	39
12-24	0.05	3.24	2.10	5.39	60	0	2.33	2.96	5.29	44
24-36	0	1.71	4.38	6.09	28	0	2.33	3.73	6.06	38
36-48	0	1.18	5.18	6.36	19	0	1.49	4.87	6.36	23

TABLE 10
EFFECT OF SULFUR ON THE REPLACEABLE BASES
(Milliequivalents per 100 grams.)

Plot 10										
Depth in inches	Before treatment					After treatment				
	K	Na	Ca+Mg	Total (S)	Na as per cent of total	K	Na	Ca+Mg	Total (S)	Na as per cent of total
0-12	0.28	2.69	2.60	5.57	48	0.08	2.02	3.65	5.75	35
12-24	0.12	3.07	2.40	5.59	55	0.05	1.35	4.15	5.55	24
24-36	0.04	2.81	3.20	6.05	46	0.02	1.57	4.62	6.21	25
36-48	0.07	2.50	3.38	5.95	42	0.05	1.73	4.35	6.13	28

Plot 19										
Depth in inches	Before treatment					After treatment				
	K	Na	Ca+Mg	Total (S)	Na as per cent of total	K	Na	Ca+Mg	Total (S)	Na as per cent of total
0-12	0.36	3.31	2.07	5.74	58	0.15	2.39	3.42	5.96	40
12-24	0.09	2.85	2.93	5.87	49	0.04	2.10	3.41	5.55	38
24-36	0.08	2.72	3.39	6.19	44	0	2.05	3.90	5.95	34
36-48	0.10	2.82	3.78	6.70	42	0	2.18	4.48	6.66	33

This method rests on the assumption that the soil contains no compounds of sodium or potassium, other than the water-soluble salts, that are soluble in ammonium chlorid solution. The fact that practically no potassium was found in the samples drawn after the materials had been applied is strong evidence in support of this assumption. It should be borne in mind, however, that when we are dealing with a soil which has a low total replaceable-base content, such as the Fresno soil, small amounts of impurities in the chemical reagents, together with only slight solubility effects, may materially affect the relative percentage of sodium found.

TABLE 11
EFFECT OF IRON SULFATE ON THE REPLACEABLE BASES
(Milliequivalents per 100 grams.)

Plot 17										
Depth in inches	Before treatment					After treatment				
	K	Na	Ca+Mg	Total (S)	Na as per cent of total	K	Na	Ca+Mg	Total (S)	Na as per cent of total
0-12	0.46	3.14	1.38	4.98	63	0.09	2.34	2.74	5.17	45
12-24	0.21	2.64	2.35	5.20	51	0.04	2.41	2.83	5.28	46
24-36	0.10	2.12	2.99	5.21	41	0.02	2.61	2.57	5.20	50
36-48	0	2.29	2.81	5.10	45	0.03	2.34	2.70	5.07	46

Plot 45										
0-12	0.30	3.09	2.54	5.93	52	0	1.53	4.48	6.01	25
12-24	0.12	2.84	3.10	6.06	47	0	2.00	4.01	6.01	33
24-36	0.00	2.05	4.65	6.70	31	0	1.85	4.91	6.76	27
36-48	0.03	2.16	4.34	6.53	33	0	1.22	5.50	6.72	18

As shown in tables 9-12 the content of replaceable monovalent base (chiefly sodium) has been decreased and the content of replaceable divalent base has been materially increased by each of the treatments that have been applied. This effect has been most marked in the upper layers of the soil. With certain of the plot this effect has been confined entirely to the first and second feet. The relationship of replaceable sodium to total replaceable base is especially well brought out by expressing the sodium as per cent of the total content of replaceable bases. In his previous work on Hungarian alkali soils Arany⁽¹⁾ brought out a similar relationship by showing the effects produced by certain treatments on the so-called alkali quotient of the soil, which quotient was determined by dividing the sum of the

replaceable sodium and potassium by the total replaceable bases. Since solubility effects and impurities in the reagents may have been involved in the sodium determinations, these data should not be considered as absolute. However, the differences found in the samples taken before and after the treatments were applied are fairly consistent. The relationship of the replaceable monovalent bases (sodium in particular) to the total replaceable bases, is a fundamentally important aspect of alkali soils, as has been emphasized in previous publications from this and other laboratories.

TABLE 12
EFFECT OF ALUM ON THE REPLACEABLE BASES
(Milliequivalents per 100 grams.)

Plot 18										
Depth in inches	Before treatment					After treatment				
	K	Na	Ca+Mg	Total (S)	Na as per cent of total	K	Na	Ca+Mg	Total (S)	Na as per cent of total
0-12	0.40	3.68	0.87	4.95	74	0.09	1.72	3.04	4.85	35
12-24	0.00	2.90	1.82	4.72	61	0.04	1.37	3.22	4.63	30
24-36	0.00	3.61	1.84	5.45	66	0.04	1.89	3.22	5.15	37
36-48	0.00	3.47	1.86	5.33	65	0.00	1.84	3.19	5.03	37

CALCIUM AND MAGNESIUM EXTRACTED WITH NH_4Cl

The solutions obtained by leaching the samples of soil with normal ammonium chlorid were analyzed for calcium and magnesium as well as for potassium and sodium. The assumption was made that the loss in water-insoluble carbonates incident to leaching with ammonium chlorid was due to the solution of normal carbonate of calcium and magnesium. If this assumption is correct, the ammonium chlorid extracts must have contained calcium or magnesium, or both, derived from carbonate forms, in amounts equivalent to the loss in CO_3 . The amounts⁸ thus calculated are recorded in tables 13 to 19, column 4. The replaceable calcium and magnesium, calculated by the method already discussed [NH_4 absorbed — replaceable (K + Na)] is given in column 5. The sum of the replaceable and the dissolved-carbonate forms subtracted from the total amounts of these bases

⁸ If the soil contains basic carbonate of magnesium, the data calculated on the basis of normal carbonate are probably too low.

found must represent still other forms of calcium and magnesium, probably silicates. Data obtained by this method of calculation are reported in column 6 of these tables.

TABLE 13
PLOT 4, EFFECT OF GYPSUM ON THE CALCIUM AND MAGNESIUM CONSTITUENTS;
AMOUNTS EXTRACTED WITH NH_4Cl SOLUTION
(Milliequivalents per 100 grams.)

	1	2	3	4	5	6
	Ca	Mg	Total Ca+Mg	Ca+Mg as carbonates	Replaced Ca+Mg [$\text{HN}_4-(\text{K}+\text{Na})$]	Ca+Mg as com- pounds other than replaceable and car- bonate forms (3-4-5)
1st ft. before treatment.....	5.42	2.02	7.44	1.56	1.10	4.78
1st ft. after treatment.....	7.87	1.79	9.66	1.60	3.17	4.89
2nd ft. before treatment.....	4.57	1.71	6.28	0.31	1.52	4.45
2nd ft. after treatment.....	6.01	1.68	7.69	0.21	2.95	4.53
3rd ft. before treatment.....	4.77	2.25	7.02	2.31	2.53	2.18
3rd ft. after treatment.....	4.96	1.91	6.87	2.33	2.32	2.22
4th ft. before treatment.....	5.42	2.49	7.91	3.12	3.22	1.57
4th ft. after treatment.....	4.30	1.84	6.14	2.80	2.28	1.06

TABLE 14
PLOT 10, EFFECT OF SULFUR ON THE CALCIUM AND MAGNESIUM CONSTITUENTS;
AMOUNTS EXTRACTED WITH NH_4Cl SOLUTION
(Milliequivalents per 100 grams.)

	1	2	3	4	5	6
	Ca	Mg	Total Ca+Mg	Ca+Mg as carbonates	Replaced Ca+Mg [$\text{NH}_4-(\text{K}+\text{Na})$]	Ca+Mg as com- pounds other than replaceable and car- bonate forms (3-4-5)
1st ft. before treatment.....	9.05	2.82	11.87	0.79	2.60	8.48
1st ft. after treatment.....	8.64	2.37	11.01	0.50	3.65	6.86
2nd ft. before treatment.....	6.29	2.49	8.78	0.22	2.40	6.16
2nd ft. after treatment.....	8.71	2.55	11.26	0.93	4.15	6.18
3rd ft. before treatment.....	14.43	4.35	18.78	12.99	3.20	2.59
3rd ft. after treatment.....	26.01	4.38	30.39	21.73	4.62	4.04
4th ft. before treatment.....	20.41	4.71	25.12	21.81	3.38	-0.07
4th ft. after treatment.....	29.16	4.74	33.90	27.02	4.35	2.53

It will be noted that in each instance a greater amount of calcium than magnesium was extracted and that with the exception of plot 4 the quantities of calcium found and of carbonate dissolved were much

greater in the third and fourth feet than in the first and second feet. On the other hand there was not a corresponding consistent relationship as regards magnesium. The data indicate that calcium carbonate is the predominant but not the only water-insoluble carbonate in this soil.

TABLE 15

PLOT 11, EFFECT OF GYPSUM ON THE CALCIUM AND MAGNESIUM CONSTITUENTS;
AMOUNTS EXTRACTED WITH NH_4Cl SOLUTION

(Milliequivalents per 100 grams.)

	1	2	3	4	5	6
	Ca	Mg	Total Ca+Mg	Ca+Mg as carbonates	Replaced Ca+Mg [$\text{NH}_4-(\text{K}+\text{Na})$]	Ca+Mg as com- pounds other than replaceable and car- bonate forms (3-4-5)
1st ft. before treatment.....	7.89	2.43	10.32	6.94	1.12	2.26
1st ft. after treatment.....	8.66	2.40	11.06	6.60	2.92	1.54
2nd ft. before treatment.....	5.60	2.36	7.96	5.06	2.10	0.80
2nd ft. after treatment.....	8.42	2.29	10.71	4.80	2.96	2.95
3rd ft. before treatment.....	20.03	4.69	24.72	19.87	4.38	0.47
3rd ft. after treatment.....	16.08	3.64	19.72	13.33	3.73	2.06
4th ft. before treatment.....	29.92	5.68	35.60	23.56	5.18	6.86
4th ft. after treatment.....	27.32	5.23	32.55	23.11	4.87	4.57

TABLE 16

PLOT 17, EFFECT OF IRON SULFATE ON THE CALCIUM AND MAGNESIUM
CONSTITUENTS; AMOUNTS EXTRACTED WITH NH_4Cl SOLUTION

(Milliequivalents per 100 grams.)

	1	2	3	4	5	6
	Ca	Mg	Total Ca+Mg	Ca+Mg as carbonates	Replaced Ca+Mg [$\text{NH}_4-(\text{K}+\text{Na})$]	Ca+Mg as com- pounds other than replaceable and car- bonate forms (3-4-5)
1st ft. before treatment.....	9.70	4.20	13.90	1.91	1.38	10.61
1st ft. after treatment.....	9.15	2.51	11.66	2.09	2.74	6.83
2nd ft. before treatment.....	8.09	4.74	12.83	1.04	2.35	9.44
2nd ft. after treatment.....	9.43	3.56	12.99	2.47	2.83	7.69
3rd ft. before treatment.....	22.62	5.06	27.68	18.55	2.99	6.14
3rd ft. after treatment.....	30.30	4.85	35.15	29.49	2.57	3.09
4th ft. before treatment.....	34.75	5.71	40.46	29.16	2.81	8.49
4th ft. after treatment.....	28.45	4.48	32.93	24.31	2.70	5.92

The calculations reported in column 6 of the tables support the view that this soil contains silicates of calcium or magnesium or both that are soluble in ammonium chlorid solution. The different plots and the various depths of a given plot differ in this regard. The upper horizon of plot 11 seems to contain considerably less soluble silicate than that of the other plots.

TABLE 17

PLOT 18, EFFECT OF ALUM ON THE CALCIUM AND MAGNESIUM CONSTITUENTS;
AMOUNTS EXTRACTED WITH NH_4Cl SOLUTION
(Milliequivalents per 100 grams.)

	1	2	3	4	5	6
	Ca	Mg	Total Ca+Mg	Ca+Mg as carbonates	Replaced Ca+Mg [$\text{NH}_4-(\text{K}+\text{Na})$]	Ca+Mg as com- pounds other than replaceable and car- bonate forms (3-4-5)
1st ft. before treatment.....	8.86	4.23	13.09	5.15	0.87	7.07
1st ft. after treatment.....	9.57	2.98	12.55	3.41	3.04	6.10
2nd ft. before treatment.....	10.15	4.99	15.14	6.41	1.82	6.91
2nd ft. after treatment.....	13.57	4.24	17.81	6.27	3.22	8.32
3rd ft. before treatment.....	38.63	8.35	46.98	40.72	1.84	4.42
3rd ft. after treatment.....	37.02	7.61	44.63	41.52	3.22	-0.11
4th ft. before treatment.....	41.53	7.03	49.46	46.09	1.86	1.51
4th ft. after treatment.....	30.87	5.18	36.05	26.82	3.19	6.04

As regards the effects of the treatments that have been applied to these plots, the data show that the extractable magnesium has been slightly decreased and the total replaceable divalent base has been substantially increased. With the exception of plot 4, which was treated with 15 tons per acre of gypsum, the data reported in column 6 of tables 13 to 19 indicate that the soluble silicate of the first foot has also been decreased. Although the methods of determination, upon the results of which these calculations are based, are not highly accurate, especially where relatively large amounts of carbonates occur, it seems probable that this black-alkali soil contains a small amount of some easily decomposable calcium silicate which is acted upon by the products of sulfur oxidation and acidic substances like iron sulfate and alum. The calcium of such compounds, if present, would thus be caused to play an important part in the reclamation process. The black-alkali soil near Salt Lake City, Utah, appears to contain relatively large amounts of easily decomposable silicate of calcium.⁽¹³⁾

TABLE 18

PLOT 19, EFFECT OF SULFUR ON THE CALCIUM AND MAGNESIUM CONSTITUENTS;
AMOUNTS EXTRACTED WITH NH_4Cl SOLUTION
(Milliequivalents per 100 grams.)

	1	2	3	4	5	6
	Ca	Mg	Total Ca+Mg	Ca+Mg as carbonates	Replaced Ca+Mg [$\text{NH}_4-(\text{K}+\text{Na})$]	Ca+Mg as com- pounds other than replaceable and car- bonate forms (3-4-5)
1st ft. before treatment.....	9.89	3.80	13.69	2.91	2.08	8.70
1st ft. after treatment.....	8.43	3.58	12.01	1.75	3.42	6.84
2nd ft. before treatment.....	7.80	4.16	11.96	1.16	2.93	7.87
2nd ft. after treatment.....	7.15	3.74	10.89	1.94	3.45	5.50
3rd ft. before treatment.....	20.52	5.02	25.54	13.65	3.39	8.50
3rd ft. after treatment.....	22.30	5.03	27.33	15.85	3.90	7.58
4th ft. before treatment.....	35.32	7.25	42.57	28.85	3.78	9.94
4th ft. after treatment.....	32.16	6.24	38.40	29.77	4.48	4.15

TABLE 19

PLOT 45, EFFECT OF IRON SULFATE ON THE CALCIUM AND MAGNESIUM
CONSTITUENTS; AMOUNTS EXTRACTED WITH NH_4Cl SOLUTION
(Milliequivalents per 100 grams.)

	1	2	3	4	5	6
	Ca	Mg	Total Ca+Mg	Ca+Mg as carbonates	Replaced Ca+Mg [$\text{NH}_4-(\text{K}+\text{Na})$]	Ca+Mg as com- pounds other than replaceable and car- bonate forms (3-4-5)
1st ft. before treatment.....	6.15	4.41	10.56	0.89	2.54	7.13
1st ft. after treatment.....	8.29	3.91	12.20	0.86	4.48	6.86
2nd ft. before treatment.....	5.30	4.56	9.86	1.83	3.10	4.88
2nd ft. after treatment.....	7.35	4.22	11.57	1.96	4.01	5.60
3rd ft. before treatment.....	15.86	5.31	21.17	9.59	4.65	6.93
3rd ft. after treatment.....	15.58	5.27	20.85	10.86	4.91	5.08
4th ft. before treatment.....	16.86	4.89	21.75	14.9	4.34	2.45
4th ft. after treatment.....	26.95	5.85	32.80	23.02	5.50	4.28

GENERAL DISCUSSION

The preceding data show that under the influence of the treatments that have been applied, this soil is being transformed into a normal soil, although the transformation has not yet become complete. Now that the several treatments have brought about a substantial reduction in the content of soluble carbonate, the replacement of a considerable part of the replaceable sodium by divalent base (probably calcium) and a material reduction in the OH-ion concentration (table 20), careful management of the soil as regards the drainage conditions and irrigation practice should promote a continuation of these changes. Under these conditions the products of biological agents, acting on the calcium carbonate of the soil, will gradually bring about a further replacement of sodium by calcium, and good drainage conditions will make it possible to leach away the soluble sodium salts that are formed.

TABLE 20
EFFECT ON THE PH VALUE OF THE SOIL

Depth in inches	Plot 4		Plot 11		Plot 10		Plot 19	
	Before treatment	After treatment with gypsum	Before treatment	After treatment with gypsum	Before treatment	After treatment with sulfur	Before treatment	After treatment with sulfur
0-12	9.55	8.20	9.72	8.54	9.70	7.49	10.10	9.15
12-24	9.72	8.94	9.72	9.67	9.70	8.63	9.86	9.51
24-36	9.69	9.26	9.55	9.37	9.82	9.49	9.71	9.10
36-48	9.38	9.26	9.52	9.30	9.38	9.65	9.37	8.73

Depth in inches	Plot 17		Plot 45		Plot 18	
	Before treatment	After treatment with iron sulfate	Before treatment	After treatment with iron sulfate	Before treatment	After treatment with alum
0-12	9.77	8.85	9.70	8.88	9.86	8.78
12-24	9.52	9.25	9.62	9.54	9.70	9.19
24-36	9.37	9.17	9.44	9.37	9.37	9.04
36-48	9.04	8.85	8.86	8.73	9.35	8.79

As stated already the application of gypsum brings about two important chemical reactions in black-alkali soils; namely, the conversion of (a) sodium carbonate into sodium sulfate and calcium carbonate, and of (b) sodium-exchange compounds into calcium compounds and sodium sulfate. Neither of these reactions can go to

completion unless the soluble sodium salts are leached out. Moreover, these reactions take place simultaneously. Hence, the amount of gypsum required is dependent upon the content of both sodium carbonate and replaceable sodium, and, as suggested above, it may be necessary to leach the soil to remove the soluble products. It is interesting to note in this connection that Loughridge⁽¹⁹⁾ pointed out as early as 1897 that from two to three times as much gypsum should be applied as is indicated by the soluble carbonate content of the soil. The reason for this fact was not known at that time.

The important reactions which take place when sulfur undergoes oxidation in alkali soils were recently discussed by Samuels.⁽²⁰⁾ Just as is the case with gypsum, the sulfur-oxidation product (sulfuric acid) reacts with soluble carbonate and sodium-exchange compounds simultaneously. Calcium carbonate, if present, is also acted upon, and probably certain calcium silicates as well. As shown by Samuels, the intermediate reactions are complex. They ultimately lead, however, to the neutralization of the alkaline conditions of the soil by converting the soluble carbonate into sulfate and bicarbonate and the sodium-exchange complex into calcium compounds through the effect produced on calcium carbonate and silicate. The soluble salts can then be leached out.

That sulfur brings about an activation of the water-insoluble calcium compounds is possibly the most fundamentally important factor connected with its action on an alkali soil. This phase of the question has been discussed in previous publications from this laboratory,^(13, 17, 20) but its importance justifies further emphasis. Fortunately, American alkali soils usually contain an abundance of calcium carbonate. This, however, is not true of certain important alkali areas of Europe. With the latter it is not probable that the application of sulfur will be satisfactory unless lime is also applied.

It is probable that the chemical changes that have taken place in plot 19, as regards both carbonates and replaceable bases, were produced by the joint action of the manure that was applied in 1922 and the sulfur applied in 1925, but the proportion of the changes that was produced by each of these materials can not now be determined. It seems that the major part of the reactions was caused by the sulfur, since analyses, not reported herein, failed to reveal any pronounced change in the water-soluble carbonate of this plot until several months after the sulfur was applied. Moreover, barley, sown for two successive years after the manure had been applied but before sulfur was applied, failed to germinate over most of this plot.

However, it is not until the soluble carbonate has been largely removed that crops like barley and alfalfa will grow on this soil and the decomposition of soluble carbonate goes hand in hand with reactions involving the exchange complex.

The decomposition products of the manure probably initiated the necessary chemical reactions and the oxidation product of the sulfur carried them further towards completion. The manure underwent rapid decomposition indicating active micro-biological action.⁹ It is also of interest that the rate of sulfur oxidation on this plot, as shown by evidence of sulfate formation and the germination and growth of alfalfa sown only three months after the sulfur was applied, has been especially active. Probably the micro-organisms contained in the manure and the chemical and physical effects produced by its decomposition were conducive to the rapid oxidation of sulfur.

An understanding of the chemical effects of iron sulfate and alum necessitates giving first consideration to hydrolysis. These compounds are acidic by virtue of the fact that they undergo hydrolysis, one of the hydrolytic products of each being sulfuric acid. It is the hydrogen ion thus formed that is responsible for the marked effect of these materials. It is well known, of course, that carbonates are decomposed by soluble aluminum salts with the evolution of CO_2 and the precipitation of aluminum hydroxid. As to the effect of aluminum salts upon the base-exchange constituents, Kelley and Brown⁽¹⁴⁾ showed that when a dilute solution of aluminum chlorid is added, the replacement of soil bases is brought about by the hydrogen ion formed by hydrolysis and not by the aluminum ion. In addition to these effects it is well known that aluminum and iron salts produce marked flocculation of soil colloids.

It follows from the preceding that the application of alum will bring about a decomposition of carbonates and the transformation of the sodium-exchange complex into calcium compounds, very much as is the case where sulfur is applied. The determination of the water-soluble constituents reported in table 5 and the replaceable bases shown in table 12 fully confirms this view. The aluminum hydroxid formed by hydrolysis was probably precipitated colloiddally by the electro-negative soil colloids. Later, when the soil dried out, the aluminum hydroxid probably passed into aluminum oxid by dehydration and thus became a relatively stable and inert component of the soil.

⁹ Since micro-organisms are known to be more or less active in many black-alkali soils, carbon dioxid must be formed therein, notwithstanding the claim (3, 4) that carbon dioxid is non-existent in this kind of soil.

While iron sulfate probably brings about a partial precipitation of the soluble carbonate as iron carbonate, the fundamentally important chemical reactions produced by it are largely those involving the action of the hydrogen ion. In this case also, as shown in tables 4, 7, 8 and 11, the hydrogen ion decomposed soluble carbonates and converted sodium-exchange complex into calcium compounds through the intermediate agency of calcium carbonate. The ferrous hydroxid formed by hydrolysis was absorbed by the soil colloids and was later oxidized into the ferric form and thus became essentially inert.

Thus it will be seen that there is a fundamental similarity in the reactions produced by oxidizing sulfur, alum and iron sulfate. The rates at which these substances react, however, are widely different. Sulfur, being dependent upon biological agents for its oxidation, must necessarily react relatively slowly. Iron sulfate and alum, on the other hand, being highly soluble substances, react at once. It is probable that the full chemical effect of these last named substances is exerted as soon as they are brought into contact with the soil particles through the solvent and leaching action of water.

Soon after alum and iron sulfate were applied to these plots pronounced effects were noted in the chemical and physical properties of the soil. Although these materials were applied more than five years ago (1922), and the soil has been leached and irrigated freely since that time, there is as yet no indication of a reversal of the beneficial chemical and physical effects. The plots, although originally highly puddled and impervious, have continued to absorb water freely since these materials were applied, their tilth is good and on each of them the growth of alfalfa is excellent. The beneficial physical effects are probably due chiefly to the chemical reactions referred to above and not to the coagulation of the colloids of the soil independent of the chemical changes. When this is the case leaching will, therefore, probably not bring about a reversal of the effects, as Joffe and McLean⁽¹⁰⁾ inferred would be the case. In fact it appears to be impossible to coagulate the colloids of this soil by means of aluminum or iron salts without decomposing carbonates and altering the chemical nature of the exchange complex, and these chemical reactions are the important effects which aluminum and iron salts produce.

As stated already, each of the materials that have been applied has reacted with the carbonates and the base-exchange complex of the soil. It does not follow, however, that the amount of chemical change which these constituents have undergone, is a reliable measure of the chemical efficiency of the applied materials. In addition to the effects

produced by these materials, the calcium content of the irrigation water and carbon dioxid formed by micro-biological agents and the growth of crops have taken part in the chemical reactions. Moreover, there has been some calcium and sulfate lost by leaching and absorbed by the crops. Finally the fact that this soil is extremely variable, as was shown previously,⁽¹¹⁾ should also be borne in mind. Since the magnitude of these various factors is unknown, it is not possible to determine the precise chemical efficiency of the applied materials. The data, however, clearly establish the qualitative nature of the reactions.

From a practical standpoint, the data also suggest that it is not necessary to apply any of these materials in amounts equivalent to the total soluble-carbonate and replaceable-sodium content of the soil. When materials of these kinds are applied the reactions will bring about a reduction in the OH-ion concentration in consequence of which micro-biological action will be stimulated. This latter will lead to the formation of carbon dioxid and the gradual solution of calcium minerals in the soil, which in turn will react with the base-exchange complex and ultimately serve to stimulate plant growth. When the chemical reactions produced by these various means have reached the point where a crop like alfalfa can be grown satisfactorily, it seems probable that the remaining portion of the needed chemical change can be effected through proper management of the soil. By plowing down green manures or farm manures and the liberal use of irrigation water, the calcium minerals of the soil will gradually react with the exchange complex and the replaced sodium will be leached out. Thus the soil constituents will ultimately become essentially normal in composition.

As was pointed out above the growth of crops has been markedly stimulated by the application of these materials. The most pronounced effect has been in those cases where the chemical changes in the soluble carbonates and the base-exchange constituents have been the greatest. As will be seen by reference to the crop records reported in a separate paper,⁽¹⁸⁾ there is good agreement between the effects on crops and the chemical changes referred to above. On the other hand, the untreated check plots of these experiments have not produced satisfactory yields. In fact barley and alfalfa still fail to grow satisfactorily on the greater part of the check plots, whereas large yields of alfalfa are being obtained from the plots that have been discussed in this paper.

SUMMARY

The application of gypsum, sulfur, iron sulfate and alum has produced important chemical changes in the black-alkali soil near Fresno, California. With each of these materials the chemical reactions have involved the soluble carbonate and the exchange complex of the soil. It was found that gypsum has precipitated the soluble carbonate as calcium carbonate in accordance with theory, while the other materials have either decomposed carbonate or else converted it into bicarbonate. Simultaneously with the effect on soluble carbonate, the exchange complex has been acted upon.

The effect of gypsum is dependent on its soluble calcium, while sulfur, iron sulfate and alum are effective because of the H ions that are formed. The acid formed by the oxidation of sulfur, or the hydrolysis of iron sulfate and alum, dissolves calcium carbonate, and possibly other minerals, and thus brings calcium into solution. As a result the sodium content of the exchange complex is decreased and the calcium content is increased. In consequence of these chemical transformations the physical conditions of the soil have been markedly improved and the growth of crops has been pronouncedly stimulated.

The theoretical and practical aspects of the black-alkali soil problem have been discussed.

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